

Analyzing the Corrosion Resistance of Ni-Shield 200 Coatings at Different Temperatures When Exposed to Sulphuric Acid

Alex Hussinger

Advisor: Professor Blair London

Industry Sponsor: Scoperta Inc.

Materials Engineering Department

California Polytechnic State University

Corrosion of Ni-Shield 200 Alloy

Approval Page

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Author: Alex Hussinger

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CAL POLY STATE UNIVERSITY

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Prof. Blair London

Faculty Advisor

Signature

Prof. Trevor Harding

Department Chair

Signature

Abstract

Six steel samples each were twin wire arc sprayed with Hastelloy C-276 or Nickel-Shield 200 coatings approximately 0.020" thick. These samples were then cut into 3" by 3" squares. A 2" diamond grit hole saw was used to abrade and polish to a smooth surface a ring in the middle in order to get an O-ring mechanical seal. The samples were then weighed and loaded into a jig that started from the bottom up with a stainless steel plate, then the sample, then a Viton O-ring, a 3/4" thick glass plate with a 1 3/4" hole cut in it, another O-ring, and then another stainless steel plate. The plates were bolted together tightly in the corners. This setup was designed to expose only the top surface of the coated sample to sulphuric acid, which is an accurate representation of an application of the coating. The samples were tested with 98% concentrated sulphuric acid at room temperature, 100°F, and 200°F over a period of 2 weeks. The corrosion rates could not be calculated accurately due to leakage of the sulphuric acid onto the sample. However, there were macroscopic signs of corrosion product on the Ni-Shield 200 samples that were not present on the Hastelloy C-276 samples. The microstructures of both samples also showed signs of surface attack. While a precise corrosion mechanism could not be identified, the Ni-Shield 200 sample did react with the sulphuric acid enough to warrant further study into its mechanisms and methods.

Keywords: Corrosion, Nickel Shield 200, Passive, Thermal Spray, Coating, Materials Engineering, Pitting, Sulphuric Acid, Hastelloy C-276

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Introduction

Corrosion is a serious problem in the modern world. In 2002, a NACE (National Association of Corrosion Engineers) study revealed that the cost of corrosion in the US for that year alone was a staggering \$276 Billion, or about 3% of the nation's GDP^[1]. Although not all of this is currently preventable, most of it could be reduced or eliminated with a better understanding of how corrosion works and with the implementation of better prevention methods.

The reason corrosion is such a problem is that most pure metals and alloys are not thermodynamically stable under standard conditions^[2]. At ordinary temperatures, the metal atoms want to return to an oxide or some other chemical structure instead of staying as a pure metal, which is usually only stable at the higher temperatures required to smelt ore. What this means is that most metals are constantly corroding all the time, but usually so slowly so that it is almost impossible to notice. The reason for this is that while metals are not thermodynamically stable at ambient temperatures, they are kinetically stable. This means that even though the reaction is spontaneous, it is proceeding so slowly that it is almost like the reaction is not occurring at all. However, that can change depending on the surrounding environments. The presence of certain elements or compounds can dramatically accelerate the rate of corrosion to the point where it is a serious structural problem. These can range from moisture in the air to seawater to concentrated acids or bases.

Galvanic Corrosion

There are many kinds of corrosion, but the most important is galvanic corrosion. Galvanic corrosion occurs when two different metals or the same metal with two different potentials are exposed to an electrolyte and are electrically connected (Figure 1). What this

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creates is essentially a closed circuit battery between the two materials as one is oxidized and the other is reduced, which requires flowing electrons.

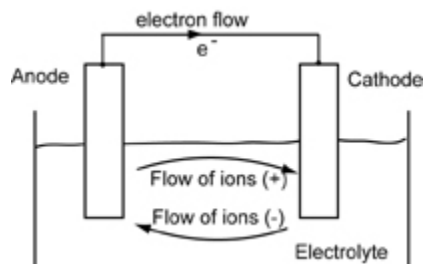


Figure 1: Basic galvanic corrosion cell, showing all 4 constituent parts ^[3]

This form of corrosion is based on having different cathodes and anodes in the material. The cathode is the region where the metal is reduced, and the anode is where the metal is oxidized. In order for galvanic corrosion to occur, the anode and cathode must be electrically connected so that the electrons removed at the anode can be transported to the cathode. Also, the two regions must either share an electrolyte that can transport ions in solution between them, or be exposed to an aqueous solution that can supply alternative ions for a reduction reaction instead ^[4].

Which metal is the cathode and which is the anode (or where the anode and cathode forms on the same material) depends on the electrical potential of their oxidation reaction with respect to the standard hydrogen electrode. This potential refers to how thermodynamically favorable the reaction is under the current conditions ^[5]. In a standard electrolyte setup (Figure 1) the reaction with the higher potential will be the cathodic reaction while the reaction with the lower potential will be the anodic reaction.

However, often there is only one metal in use. In that case, the cathodic reaction is usually either the reduction of hydrogen ions into hydrogen gas, or the reduction of hydroxide ions into water. These cathodic reactions consume the electrons produced by the anodic reactions, and can therefore drive the corrosion of a single metal. These reactions can occur anywhere on the surface of the material, as the localized cathodic sites can change over time due to small variations in potential at individual points on the surface.

All four elements (anode, cathode, electric circuit between them and ion path between them) work together to produce a basic corrosion cell. Negatively charged electrons removed at the anode can flow to the cathode, and positively charged ions at the anode can flow to the cathode. Even though matter is traveling from the anode to the cathode on both sides of the stream, since one flow is positively charged and the other is negatively charged, the two still combine into one circuit. This circuit has a current that can be measured in amperes, and is one way of representing a corrosion rate.^[6]

Uniform Corrosion

Where the anodes and cathodes form depends on the localized potential differences along the metal surface, and can sometimes flip or move around in a way that achieves relatively even corrosion across the entire surface. This is called uniform corrosion and occurs when the metal surface is relatively homogenous to the point where any localized potential difference is small enough that polarization is enough to neutralize it^[7]. This means that the driving force of the reaction is small enough that forming some product makes it no longer spontaneous with respect to the former cathode. This is most commonly seen in iron rust, where the entire surface is

corroded relatively evenly. However, most of the time uniform corrosion does not occur and instead we get localized corrosion, where it is focused in one area.

Localized Corrosion

Localized corrosion occurs when the anodes stay fixed. This causes the material loss to be focused in that one place, which can cause significant problems even if the overall corrosion rate is low. Localized corrosion can cause pitting or cracking (Figure 3), as the cracks cut deeply in the material and can be the cause of many mechanical failures.

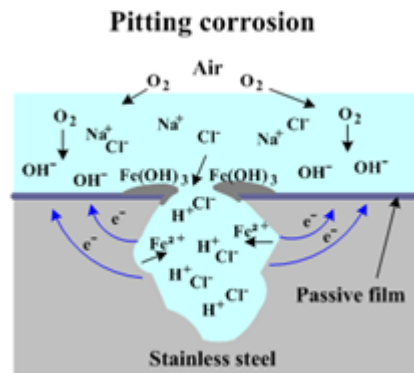


Figure 2: Diagram of pit on stainless steel, showing the different chemical reactions that occur ^[8]

The reason for this accelerated localized corrosion is because the area of the cathode is much greater than the area of the anode ^[9]. Since the overall current flow in both regions must be equal in order to maintain a circuit, this causes the current density (current/surface area) to be much larger at the anode than the cathode. Current density is directly proportional to the linear rate of corrosion at that location, as the only way to get current flow is to oxidize the metal into its ionic state. In order to sustain a large current density, more ions need to be formed over the same surface area, causing the corrosion to penetrate much deeper into the material than if it was spread out over a larger area.

Passive Layers in Corrosion

One way materials can avoid corrosion is to form a passive layer. A passive layer is a layer of corrosion product that insulates the metal from the corrosive environment, preventing any more products from being formed and therefore essentially stopping corrosion ^[10]. Passive layers are created when the product is insoluble in the environment, and layers are usually non-porous. All passive layers are non-soluble, although not all non-soluble corrosion products represent passive layers. A good example of this is iron rust, which is not soluble but does not prevent any further corrosion. Passive layers are the reason why normally highly reactive metals like aluminum or titanium can exist when they would normally corrode rapidly due to the extremely low potential of their oxidation reaction with respect to the standard hydrogen electrode.

The most common kind of passive layer is the chromium oxide passive layer that forms on the surface of stainless steels. This layer is the reason why stainless steel is “stainless”--it passively protects the iron-carbon core from corroding in most environments. However, since this passive layer requires oxygen to form, if the passive layer is ever penetrated in an anaerobic environment, corrosion of the stainless steel can proceed unhindered. There are many ways this passive layer can break down, from mechanical scraping to chipping, but the most interesting is when it breaks down chemically due to the presence of sulfuric acid.

Stainless steels are often used when corrosion is a significant problem in the application, either due to the length of time it will be used or the corrosive nature of the environment it will be exposed to. However, stainless steel is difficult to machine properly ^[11], though not impossible, as it does not chip well and can dull tools extremely quickly due to overheating.

This creates a trade-off, as machining stainless steel is costly which limits its use. However, since the passive properties of stainless steel are only needed on the surface of the material, engineers have tried to create a coating that can create a passive layer similar to stainless steel. This coating can then be applied to plain carbon steel or some other metal that has already been machined to specifications.

Coating Processes

One method of spraying the coating on is called twin wire arc thermal spraying (Figure 3). In this method, two wire forms of the coating are charged oppositely and then brought close together. Once close enough, the electrical potentials between them become strong enough to where electrical arcs form between the two wires. This heats up the metals enough to melt them, and then air is blown in to push the melted droplets onto the surface, where they cool and solidify as a coating.

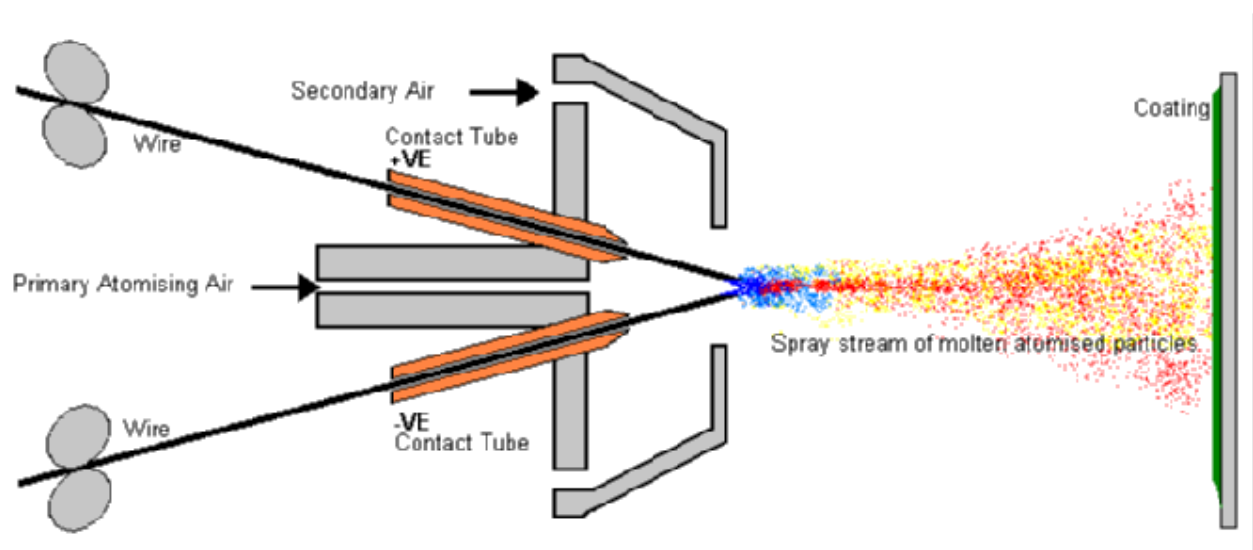


Figure 3: Schematic of the Arc Wire Thermal Spraying, showing all the steps required to melt and spray the material ^[12]

While this method does adequately coat the material, there are a number of problems with it. Because of how the coating is applied, it is usually uneven (Figure 4), which is both inefficient and potentially dangerous for pitting corrosion. There are also voids and oxide inclusions, which reduce the strength of the coating and create potential differences that can create a corrosion cell in the alloy.

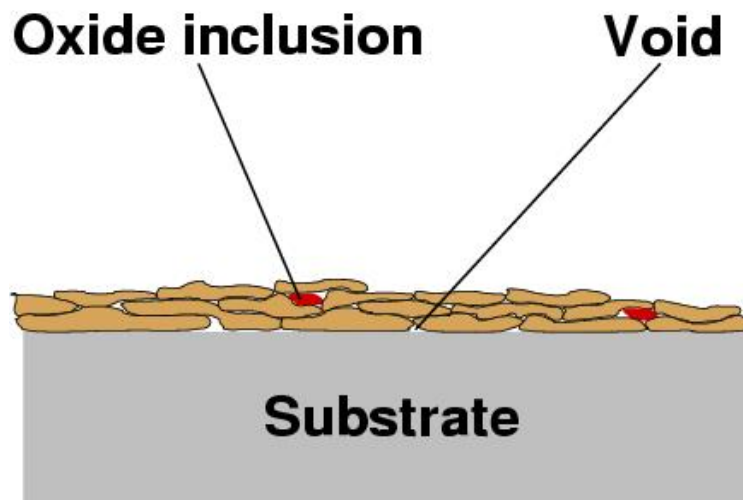


Figure 4: Schematic of the problems with thermally sprayed coatings ^[13]

Nickel-Chromium Passive Layers

One common alloy system used in thermal spray coating applications is nickel-chromium. This alloy system works because the chromium atoms react to form chromium oxide, a passive layer that is the same reason why stainless steels resist corrosion. The Nickel also reacts to form nickel oxide, another passive layer ^[14]. These two base elements, along with other alloying elements added to prevent oxidation during the thermal spraying process and to improve mechanical properties, combine to create a passive layer on the surface of the sprayed material.

Scoperta

Scoperta, my industry sponsor, is a small company now based in San Diego, California. They do research and development work dealing with thermal spray products and processes,

along with coatings for abrasive resistance and weld overlays. In this project, I will be testing how a new nickel-chromium alloy they developed called Ni-Shield 200 that is arc wire thermal sprayed onto a steel substrate will resist corrosion while exposed to sulfuric acid. I will test it at different concentrations ^[15] and temperatures ^[16] to determine how well the new alloy resists corrosions in those different environments. I will also compare its performance to the current industry standard of Hastelloy C-276 under the same conditions.

Realistic Constraints

Realistic constraints ^[17] are a part of the ABET accreditation criteria, and involve problems or issues related to real world applications that engineers have to deal with. They were created to help ensure engineers understand the larger societal consequences for their actions and to be more ethical and responsible citizens.

Manufacturability

Currently, machining parts out of stainless steel is difficult and complicated due to its tough and “gummy” nature ^[18]. However, stainless steel’s resistance to general corrosion is invaluable in many applications, and different methods of dealing with this problem have been developed. One solution is to simply machine a part out of plain carbon steel and then coat it in a stainless steel-like metal, as the passive layer is only needed at the surface. One way to coat these samples is thermal arc spraying, which involves spraying small particles of coating at high temperatures at a surface using an electrical arc. My senior project involves testing a specific alloy that is thermal arc sprayed onto a base metal. My results will determine whether or not this material and process produces an adequate corrosion resistance to concentrated sulfuric acid. If the alloy and process work, it will create a new way to add a corrosion-resistant passive layer to a machined part.

Economic

Corrosion causes large losses annually as it transforms useful metals and alloys into brittle and structurally unsound oxides. The costs of corrosion are estimated to be hundreds of billions of dollars per year in the US alone ^[19]. Much of this cost comes from preventable part failure due to corrosion, in situations where the material was either not designed for corrosion or was consciously not intended to last long, as it can sometimes be cheaper to replace a corroded part every few years than invest to prevent the corrosion in the first place. My senior project tests an alternative way to deal with general corrosion, and if it proves cost-effective it could save a lot of money each year in replacement parts.

Methodology

There are multiple ways to measure corrosion quantitatively ^[6]. The main way is to measure a linear penetration depth in inches per year. This measures how far the corrosive environment can penetrate into a material in a given period of time. The ASTM specification standard test method to measure this is to immerse a metal sample completely in a corrosive environment for two weeks, and then measure the mass loss ^[20]. You can then calculate the penetration depth by dividing the mass loss by the exposed surface area, the time it was exposed, and the density of the material. This penetration depth ranges from tens of microns per year to hundreds of millimeters per year ^[21] and depends strongly on both the material being corroded and the specific corrosive environment it is exposed to.

Experimental Setup

This ASTM standard is the basic strategy that I implemented, with a few changes. Due to how the Ni-Shield 200 coating is applied, only the coated surface of the test specimen can be exposed to the corrosive environment. This precludes a simple submersion-based test, as the

acid would likely attack the substrate at a different rate than the coating, thus rendering the results useless. Instead, I was able to construct a jig that would expose only one side of the metal to the corrosive environment, with the acid being contained by an O-ring seal (Figure 5).

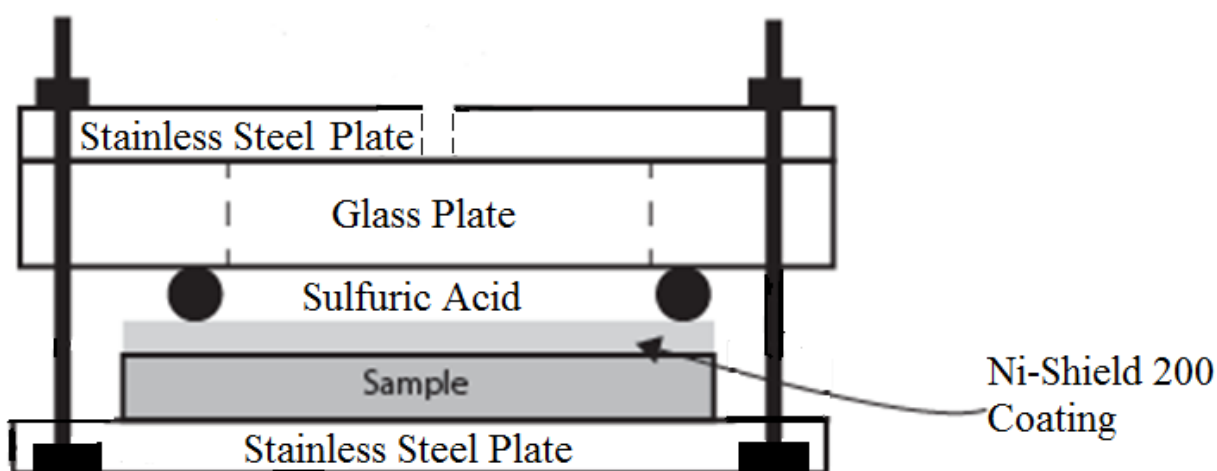


Figure 5: Schematic of the Jig Used

This jig works in a simple way. The bottom panel is a 3/8" X 4" X 4" stainless steel plate. It has four holes counter-bored into the bottom face for 1/4" hex bolts, one at each corner. This allows the plate to sit flat on top of a hot plate, exposing the maximum surface area to allow for a more even heating of the sample and the acid. On top of this plate is a 3" by 3" by 1/4" sample coated on one face with the Ni-Shield 200 coating about 500 μm thick. The sample is rotated 45° from the orientation of the base stainless steel plate to fit better on top of it. Next, a 1 7/8" outer-diameter brown Viton fluoroelastomer o-ring is placed on top, in the approximate middle of the sample. This would be directly on top of a circular polish on the coating surface, done with a 2" diamond carbide grit hole saw, in order to achieve a good seal between the o-ring and the otherwise rough as-received surface. On top of this o-ring is a 3" by 3" by 3/4" glass

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plate, with a 1 ¾" hole cut in the middle. The purpose of this plate is to increase the reservoir of acid in contact with the sample. On top of the glass plate is another stainless steel plate, the same size as, and aligned with, the bottom one. This plate has one ¼" hole drilled in each corner that lines up with the holes drilled into the bottom plate, and one 3/8" hole drilled in the center. The 3/8" hold is to provide an opening to add and remove the acid by pipette. All the parts are shown below disassembled (Figure 6), partially assembled (Figure 7) and assembled (Figure 8). I used four of these jigs at any one time, and all four were identical. Once assembled, the jigs were placed in a fume hood for safety.

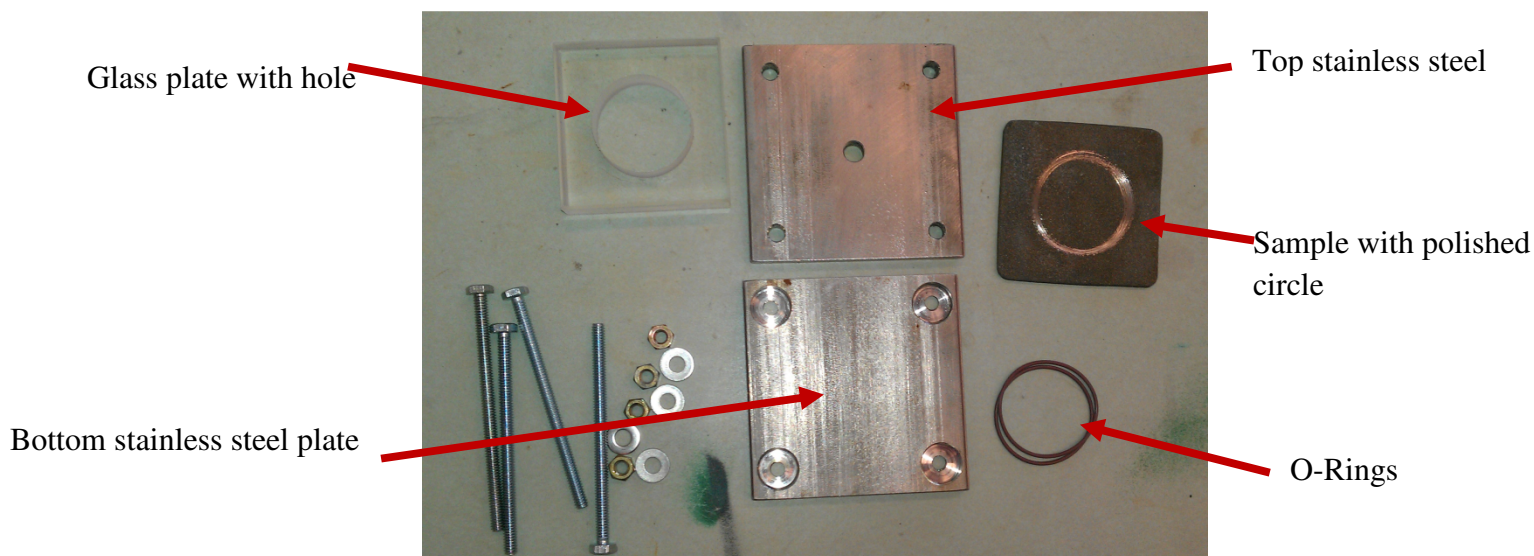


Figure 6: All the components to one jig are laid out side-by-side

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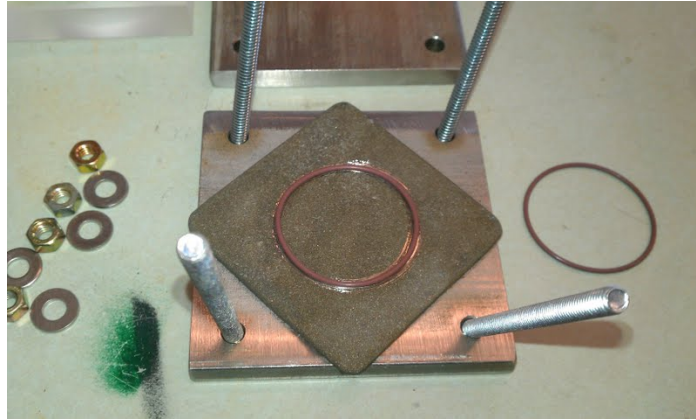


Figure 7: The bottom stainless steel plate, along with the hex bolts, sample and first o-ring are shown in this partially-assembled jig

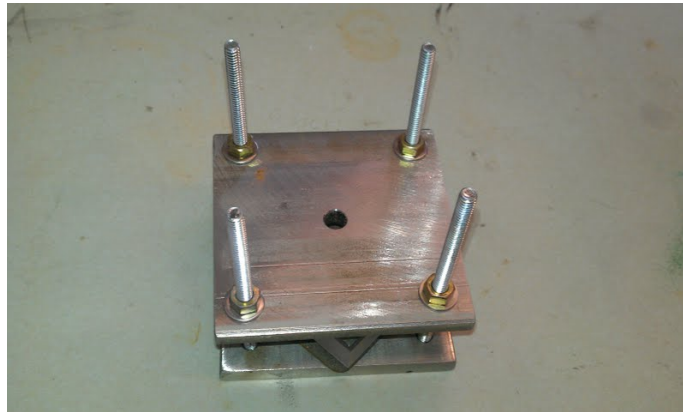


Figure 8: This is a picture of the fully assembled jig, with the hole on top where acid is added and removed visible

I was able to get parts for four jigs, allowing me to run four separate tests at once. My original plan was to test 12 different conditions, changing three factors: temperature, material, and acid concentration. The temperatures would be room temperature, measured to be 76.0°F on average, 100°F and 200°F. The materials would be Ni-Shield 200 and Hastelloy C-276, which is a current material that performs much of the same functions as Ni-Shield 200. I could then compare the results I got to the given corrosion rates under the same conditions to determine the accuracy of my test setup and method.

In order to heat the samples to the necessary temperatures of 100°F, 200°F, and room temperature, the jigs were placed onto laboratory hot plates. These hot plates originally had only numerical heating values ranging from 1-6, so with trial and error I was able to figure out what settings produced what temperatures. This was done by setting up a jig with a sample in it, filling it with water, and then gradually increasing the temperature control on the hot plate until the thermocouple stabilized at the desired temperature. While sulfuric acid and water have different heat capacities ^[22], I made the assumption that this was not significant enough to consider when setting the temperatures, which was validated once I did tests with sulfuric acid later on.

The ASTM standard ^[20] for metal corrosion testing called for an acid-to-surface area ratio of 0.2 ml/mm². This is to ensure that over the two-week test, that there is no significant buildup of corrosion product that could affect the thermodynamics of the reaction. However, after doing some calculations, I found that maintaining this ratio would require almost 10 times as much sulfuric acid as could fit in my jig at one time. So, I decided to “rotate” the sulfuric acid twice every three days to ensure there was no acid buildup. This involved pipetting out the sulfuric acid in each jig and replacing it with fresh acid.

Removing the Samples

My procedure for taking apart the jigs and cleaning the samples changed over the course of the experiment. Originally, it involved simply pipetting out the sulfuric acid as much as possible, and then taking apart the jig inside the fume hood. Each section of the jig and the sample would be neutralized with sodium bicarbonate powder, and then cleaned with tap water. However, the first time I tried this, I found that the neutralization of the sulfuric acid on top of

the sample was extremely messy and created sodium sulfate which was difficult to remove. I instead switched to using acetone on the sample first to clean off almost all of the residual sulfuric acid. This was done by using a squirt bottle filled with acetone to cover the sample, holding it above an open beaker. Once the sample was sufficiently sprayed with acetone, I switched to using de-ionized water and repeated the procedure twice to remove any last trace of acid on the surface. I then dried the samples with a paper towel.

Metallographic Procedure

To analyzing the samples, I cut them using a wet abrasive saw and mounted them in Bakelite. I then ground down the surface of the mount, going from 240 grit up to 320, 400, and 600, washing thoroughly between steps. Afterwards, I polished the samples with a 6 μ m polishing wheel using forgings solution, followed by polishes with the 1 μ m and sub-micrometer pads. I did not etch any samples, for two reasons. The first is that Scoperta told me that they could not reveal a microstructure with any of a multitude of etches. The second is that since the alloy is specifically designed to resist corrosive attack, etching could possibly corrode the sample or compromise any existing corrosion structures.

Initial Trials

After I began testing, I ran into sealing problem. The samples leaked sulfuric acid after a few days of exposure. The seal between the sample and the O-ring was not liquid-tight and this caused the acid to slowly leak out of the jig. These tests were eventually salvageable despite the leaks. However, there were two significant issues with the leakage. Since the acid was not exposed to a constant area for a constant period of time, the corrosion rate calculation that I was planning was no longer possible. Also, since the acid was then in contact with the substrate

metal rather than a corrosion-resistant coating, there was a second corrosion reaction occurring that changed the mass of the sample, also preventing the corrosion rate calculations.

Fixing this problem was difficult given how I polished down the original ring in my sample. By using a diamond grit hole saw, the polished surfaces were by their nature inconsistent and uneven. I eventually resorted to polishing multiple rings on one sample, each slightly offset from each other around one main one. This increased the area of the polish enough to improve the seal more than the initial polish, but in the end was still not enough to prevent leaks more than 48 hours into testing.

The reason for the leakage was most likely because I under-estimated how porous the samples were when planning my procedure out. Since I only polished the Ni-Shield 200 or the Hastelloy C-276 coatings rather than polishing all the way down to the base metal, what looked like a polished surface was really still porous enough to leak acid, though slowly over time.

Due to time constraints, I was unable to create a more effective solution to the leakage problem in time for my two-week tests, so I decided to continue adding sulfuric acid consistently over time in order to keep the surface constantly exposed. While this would prevent the quantitative corrosion rate calculation, it would still allow me to analyze the surface for evidence of corrosion reactions.

Corroded Surface Analysis

Since the corrosion rate calculations were ruined, I switched to more qualitative analysis of the samples. This included taking metallographic images of the cross-sections of the exposed samples, along with simple observations about their conditions and macroscopic appearances.

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The most immediate observation was that there was a buildup of corrosion product on the surface of the samples before cleaning. This product was only present on the Ni-Shield 200 coated samples, and is different depending on the testing temperature. For the room temperature and 100°F samples, this product was green and relatively thick (Figure 9). This product looked to be similar in nature to the more solidified green substance on the edges of the jig, only less concentrated, resulting in a lighter green color.



Figure 9: 100°F sample showing green corrosion product outside the continuously exposed area and the lighter green color inside the continuously exposed area

On the other hand, on the 200°F samples, the substance is yellow and aqueous (Figure 10). It appears in roughly the same places as the green corrosion product does on the lower temperature samples, though it is more concentrated in the continuously exposed area.

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Figure 10: 200°F sample showing yellow substance concentrated in the continuously exposed area. The area outside the O-ring originally was in contact with acid but it dried up during testing

These substances were exclusive, meaning that neither appeared when the other did.

Also, both substances could be washed off with acetone or water. I was not able to determine the chemical composition of these compounds due to time and material constraints, though since the samples were exposed to concentrated sulfuric acid, the yellow substance is most likely some form of concentrated sulfur.

Looking at the cleaned samples, there is also significant macroscopic evidence of a corrosion reaction on the Ni-shield 200 samples regardless of temperature (Figure 11). There is a clear color and texture difference between the three regions, indicating that exposure to concentrated sulfuric acid had a lasting effect on the coating.

Corrosion of Ni-Shield 200 Alloy

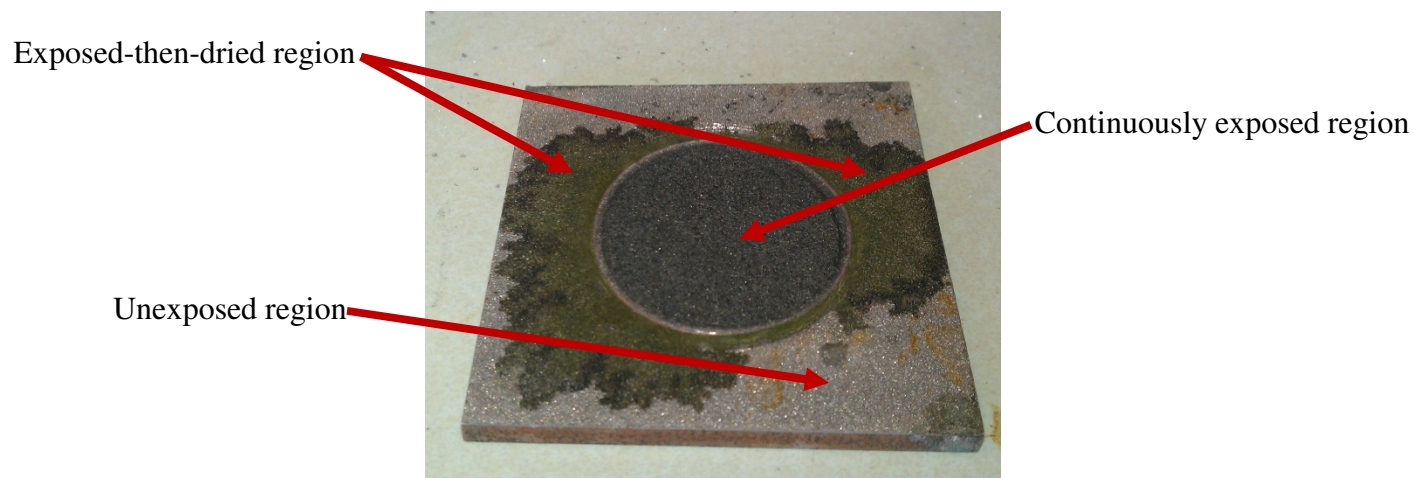


Figure 11: Cleaned 200F Ni-shield sample showing three distinct regions—the continuously exposed center, the unexposed outer edges, and the exposed-then-dried regions in between

The constantly exposed area in the middle circle is a different color than the unexposed areas around the edges. The black-yellow compound between these two sections is where acid leaked out but eventually dried up. This sort of coloration is not present on the Hastelloy C-276 samples (Figure 12), where there is almost no difference between the exposed and unexposed sections.

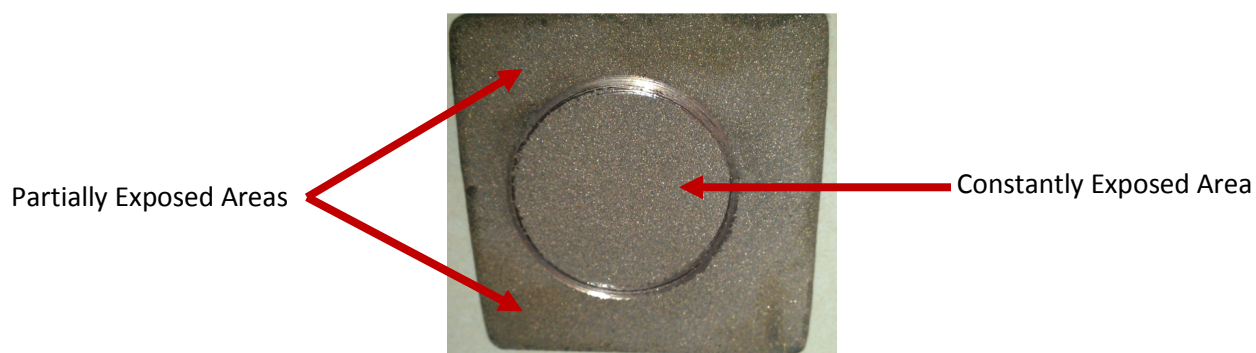


Figure 12: Cleaned Hastelloy C-276 sample after 1 week of acid exposure. Unlike the Ni-Shield 200 samples, there was little if any visual difference between the exposed and unexposed regions.

Metallographic Results

Finally, I looked at a section of the coating with an optical microscope in order to identify any localized corrosion occurring on the surface and look to see if there was any penetration of the coating towards the base material. I did this by comparing the as-received samples (Figures

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13 & 14) to the tested ones (Figure 15-18), looking for any difference in the texture of the sample surface and void concentrations or alignments in the coating itself. All micron bars are 250 μm long.

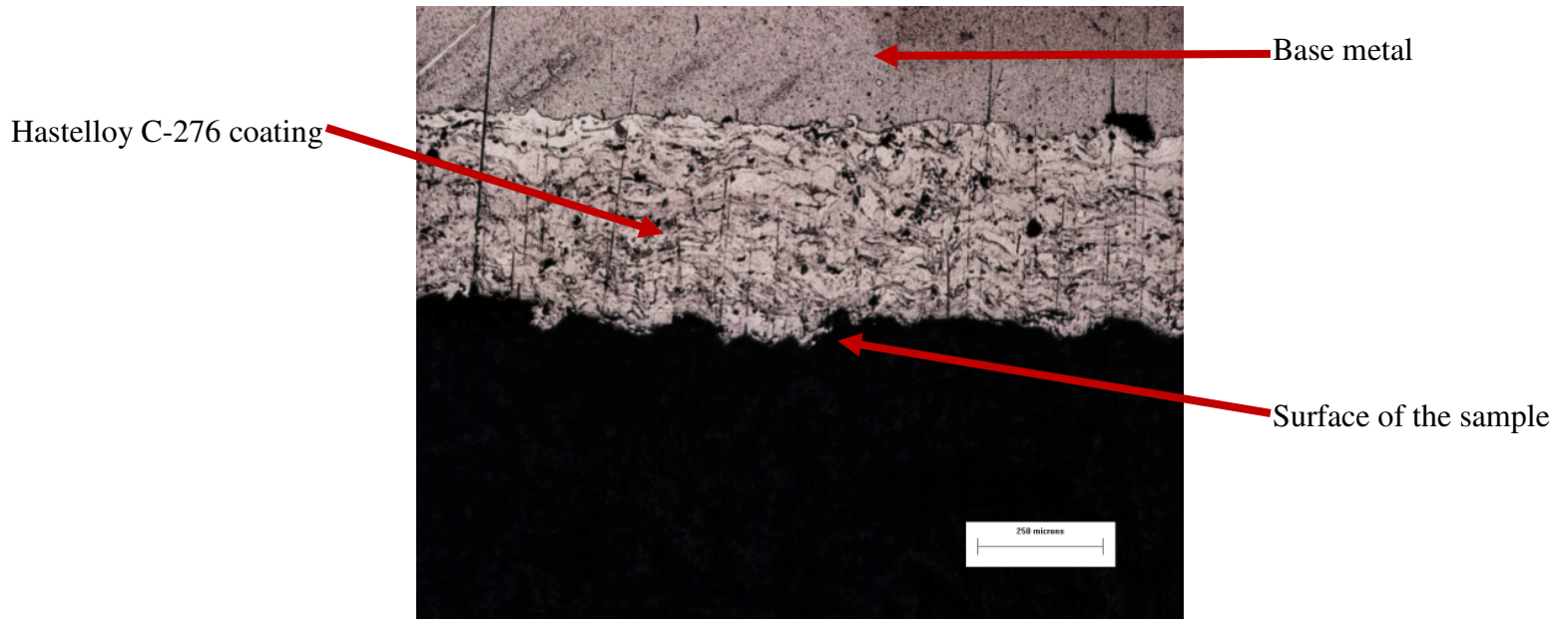


Figure 13: Hastelloy C-276 As-received 50X unetched

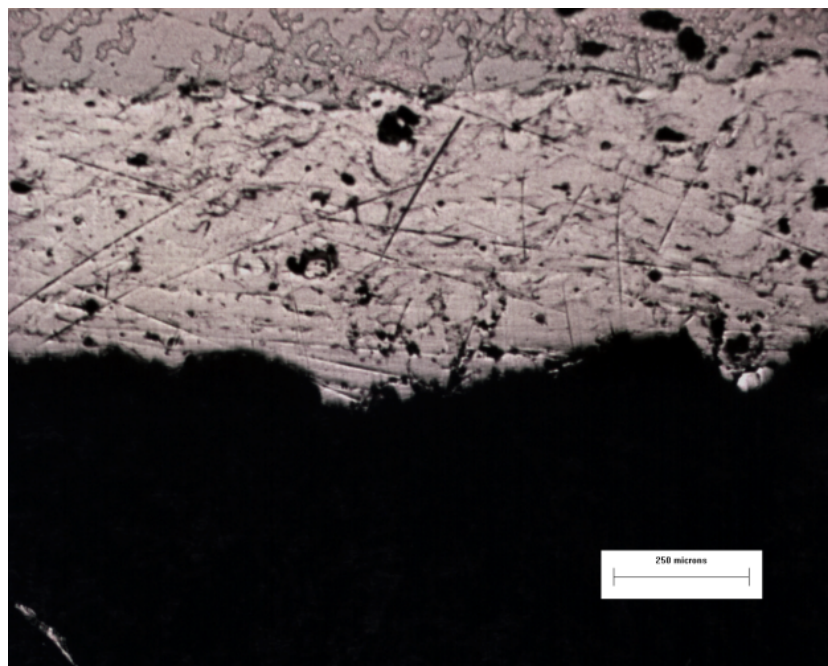


Figure 14: Ni-Shield 200 as-received 50X unetched

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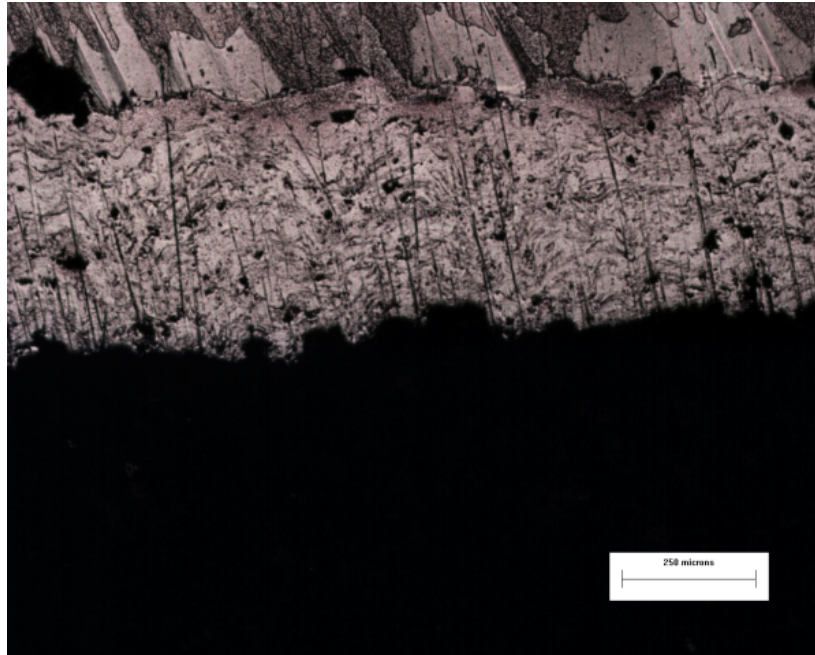


Figure 15: Hastelloy C-276 2 weeks 98% RT 50X unetched

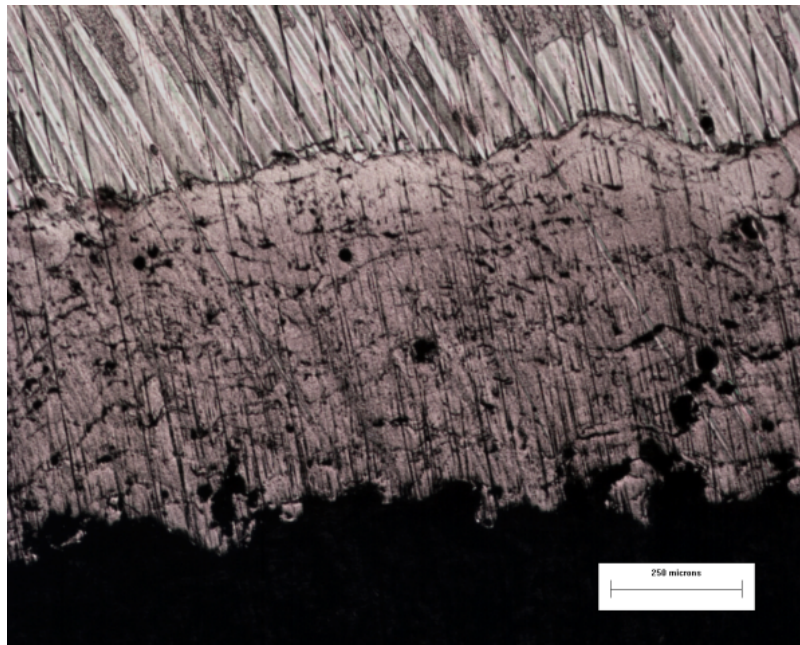


Figure 16: Ni-Shield 200 2 Weeks 98% RT 50X unetched

Corrosion of Ni-Shield 200 Alloy

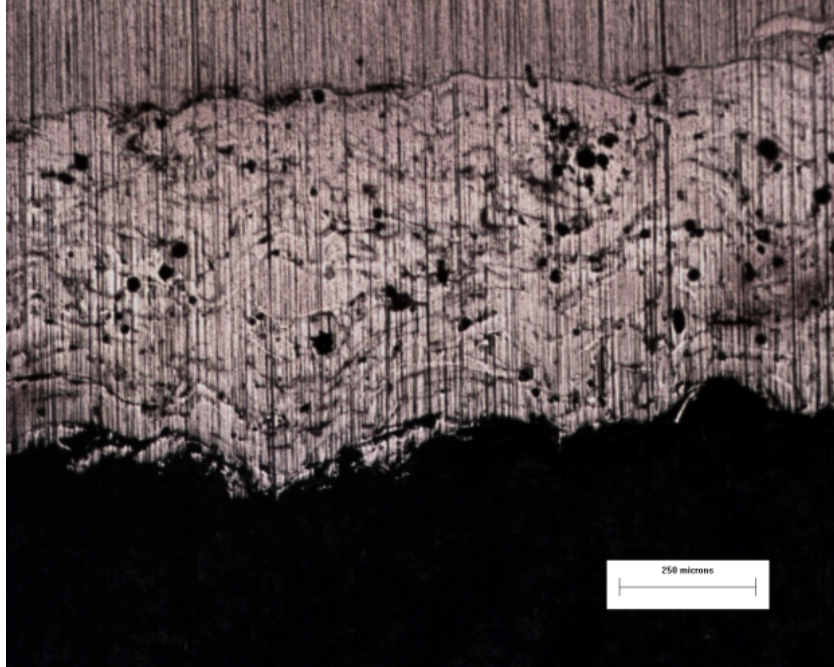


Figure 17: Ni-Shield 200 2 Weeks 98% 100F 50X unetched

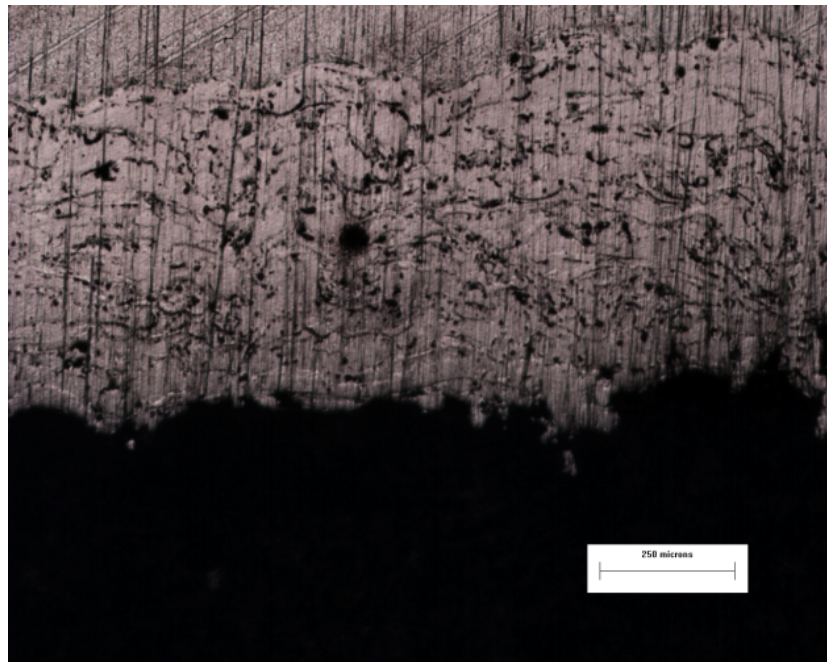


Figure 18: Ni-Shield 200 2 Weeks 98% 200F 50X unetched

For both coating alloys, there is a clear difference between the tested and as-received samples, mostly related to how the surface looks. In both coatings, the as-received surface is much smoother than in the tested surfaces, though this is clearer in the room temperature Ni-

Shield 200 samples than for the elevated temperature ones. None of the samples showed any signs of deeper coating penetration.

Discussion

For the Ni-Shield 200 samples, the corrosion product suggests that there was a corrosion reaction taking place. The fact that this product's color is temperature dependent and exclusive also suggests that the reaction depends on the temperature. Different components react more favorably at 200°F than at 100°F or room temperature. This could be a sign of de-alloying corrosion in the Ni-Shield 200 sample, with the lower temperature samples causing a different alloying element to react more favorably than at a higher temperature, leading to the different colored corrosion product. However, this cannot be determined with the data collected. I was not able to determine experimentally which elements are reacting, although I theorize that since the green corrosion product was much more common and darker outside of the O-ring and off the sample, that it was iron-based. This is because away from the sample, the acid was exposed not to the Ni-Shield 200 coating, but rather than substrate material, which was a high-strength steel. Another possibility is that the iron itself is not corroding, but merely serving as a catalyst for another reaction that produces the green substance in the low-temperature Ni-Shield 200 samples.

As for the Hastelloy C-276 sample, while there was no immediately obvious corrosion product, the microstructure was similar enough to the Ni-Shield 200 sample that I cannot say that there was no corrosion reaction. It is entirely possible that the corrosion reaction was just less macroscopically obvious. Like the Ni-Shield samples, the microstructure showed more potential

pitting sites after exposure, suggesting that there was a localized attack, and the resulting ions could have simply stayed dissolved in the sulfuric acid and removed when I rotated the acid.

Conclusions

1. Sulfuric Acid reacts with the Ni-Shield 200 alloy to produce a colored substance that changes depending on the temperature.
2. The microstructure of both coatings suggest that some kind of surface reaction took place, despite no evidence of deeper corrosion penetration

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